

Oxidation catalysis over functionalized metalloporphyrins fixated within ultralarge-pore transition metal-doped silicate supports

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Amine-functionalized metalloporphyrins stably fixated on well-defined ultralarge-pore Nb-doped silicates provided excellent catalytic oxidation activity for bulky substrates.

Numerous efforts have focused on fixating enzyme-mimic metalloporphyrin catalysts to prevent self-oxidation of the active centers and to achieve easy recovery of the catalysts.^{1,2} Conventional supports for metalloporphyrins include polymer resins, amorphous porous silicas, layered clays and zeolites.² Leaching of the porphyrins from conventional supports and steric hindrance of the catalyst due to matrix pore geometry represent major impediments to the development of effective heterogenized metalloporphyrin catalysts. To prevent distortion of the porphyrin macrocycles and to facilitate the diffusion of reactants and products in catalytic reactions, it would be ideal to employ an inorganic support with a well-defined pore structure having pore openings > 2 nm. MCM-41 silicate³ with its unique hexagonally-packed mesoporous structure represents an attractive host for supporting the large metalloporphyrin molecules.^{4,5} A highly active oxidation catalyst has been prepared by anchoring of Ru-porphyrins *via* axial nitrogen ligands to the surface of MCM-41 modified with 3-aminopropyltriethoxysilane.⁴

Our laboratory has successfully synthesized novel transition metal oxide analogs of MCM-41 (*e.g.* Nb-TMS1 and Ta-TMS1) using a covalent linkage between the amine surfactant molecules and the transition metal precursors to ensure strong interaction between the templating agents and the inorganic species during the self-assembly process.⁶ In this study, we have introduced transition metal dopants into the MCM-41 silicate framework to provide distinct sites for covalent bonding with the intentionally chosen NH₂ substituents on porphyrin macrocycles. This strategy effectively fixates the porphyrins without engaging their metal centers, leaving the latter accessible as active sites for oxidation catalysis. This technique is different from previous reports, which employed MCM-41 grafted with bulky compounds for ligand bonding with porphyrins,⁴ or involved encapsulation of porphyrins through hydrothermal synthesis or ion-exchange *via* hindered diffusion in MCM-41 with relatively small mesopore size (22–24 Å).⁵ By directly anchoring the porphyrin molecules onto the pore walls, steric

effects associated with the support structure can be minimized. The importance of active site accessibility is further illustrated in this study, which presents a first investigation on the effects of pore size and porphyrin loading on the conversion of bulky substrates during oxidation catalysis.

Nb-doped mesoporous silicates NbSil-R (where R represents the precursor Si-to-Nb atomic ratio) were synthesized by mixing an aqueous cetyltrimethylammonium bromide (CTAB) surfactant solution with a 10 wt% aqueous tetramethylammonium silicate solution, followed by the addition of niobium ethoxide.⁷ To increase the pore size of Nb-doped silicates, a mixture of cationic and neutral surfactants was used in the derivation of ultralarge-pore NbSi4-R.† Both NbSi4-R and NbSil-R gels were washed with ethanol and water, filtered and calcined at 540 °C in air for 6 h for surfactant removal. To examine the effect of support microstructure on catalytic activity, an amorphous Nb-doped silica gel was synthesized by sol-gel processing of tetraethoxysilane and niobium ethoxide under acidic conditions in the absence of surfactant templating agents. Iron porphyrins were introduced to the various calcined Nb-doped silicate supports by stirring in CHCl₃ for 24 h at room temp. The amine-functionalized iron porphyrins, Fe(III)T_{NH₂}PPBr, were prepared using a modified literature procedure.⁸

X-Ray diffraction (XRD) patterns illustrated the hexagonally-packed pore structure of our Nb-doped mesoporous silicate samples.⁷ There was negligible hysteresis in the adsorption-desorption isotherms of NbSil-5.4 and NbSi4-20, and narrow BJH (Barrett-Joyner-Halenda) pore size distributions centered at 24 and 33 Å (Table 1) were noted for these two samples, respectively. NbSil-5.4 and NbSi4-20 possessed BET (Brunauer-Emmett-Teller) surface areas of 1140 and 864 m² g⁻¹, respectively. By contrast, the amorphous Nb-doped SiO₂ sample had a type I isotherm characteristic of microporous materials (pore size < 20 Å) and a BET surface area of 557 m² g⁻¹.

The diffuse-reflectance UV-VIS spectrum of the supported FeT_{NH₂}PPBr catalysts showed a broad Soret absorption band at 420 nm, indicating the presence of iron porphyrins in the mesoporous matrix. The appearance of the Q band implies no distortion of the conjugated porphyrin plane⁹ in the large pore

Table 1 Oxidation over supported or unsupported FeT_{NH₂}PPBr catalysts under ambient conditions^a

Support	Nb (wt%)	Fe ^b /mg	Surface area/m ² g ⁻¹	Pore size/Å	Substrate	Conversion ^c (%)	Selectivity			TON/mol (mol Fe) ⁻¹	Duration/h
							Oxide	1-ol	1-one		
—	—	0.69	—	—	Cyclohexene	100	79.4	13.3	7.3	40	2
NbSil-5.4	7.72	0.75	1140	24	Cyclohexene	86	58.2	25.1	17.7	32	2
NbSi4-20	6.00	0.14	864	33	Cyclohexene	85	78.9	12.1	9.0	170	2
—	—	0.14	—	—	Cyclooctene	85	100	—	—	170	5
NbSil-5.4	7.72	0.75	1140	24	Cyclooctene	57	100	—	—	21	5
NbSil-11.4	3.64	0.36	1477	23	Cyclooctene	42	100	—	—	33	5
NbSi4-20	6.00	0.14	864	33	Cyclooctene	98	100	—	—	196	5
Nb-doped silica gel	8.60	0.36	557	< 20	Cyclooctene	14	100	—	—	11	5

^a Reaction conditions: 1 ml substrate, 4 ml CH₂Cl₂ and 0.5 mmol iodobenzene. ^b Total Fe content from unsupported porphyrin catalysts, or from 100 mg of supported porphyrin catalysts. ^c Conversion was determined by GC and based on moles of iodobenzene formed during the reaction in air.

opening of our mesoporous support. The mesostructure of the Nb-doped mesoporous silicates was preserved upon FeT_{NH₂}PPBr loading, as indicated by XRD. In addition, the absence of XRD peaks associated with iron porphyrin crystallites demonstrated that the iron porphyrins were highly dispersed in the mesoporous matrix. N₂ adsorption–desorption analyses confirmed that the iron porphyrins were loaded within the pore channels of the Nb-doped mesoporous silicates. For example, FeT_{NH₂}PPBr/NbSi4-20 has a lower BET surface area (666 m² g⁻¹), pore volume (0.89 cm³ g⁻¹) and average pore size (32 Å), compared to the unloaded NbSi4-20 support (864 m² g⁻¹, 1.14 cm³ g⁻¹, 33 Å).

The heterogeneous metalloporphyrin catalysts were tested at ambient conditions in a 25 ml batch micro-reactor (Table 1). Epoxidation of cyclohexene over FeT_{NH₂}PPBr/NbSil-5.4 gave a total conversion of 86% after only 2 h. In addition to cyclohexene oxide, cyclohex-2-en-1-ol and cyclohex-2-en-1-one were found as by-products possibly *via* allylic oxidation. Allylic oxidation might be initiated by O₂, resulting in cyclohexenyl peroxy radicals.¹⁰ Allylic oxidation has also been observed during cyclohexene epoxidation over polymer-supported iron porphyrin catalysts, which yielded cyclohex-2-en-1-one as the main product.¹¹ In comparison, significantly greater selectivity to cyclohexene oxide (58.2%) was achieved with our supported catalyst. This might be attributed to faster diffusion of the cyclohexene oxide products out of the mesoporous structure, thus alleviating further oxidation. The unsupported metalloporphyrin catalysts provided a faster reaction rate and produced an even better epoxide selectivity (79.4%) since there were no steric hindrance effects associated with substrate diffusion. We found that the use of a Nb-doped silicate support with larger pores greatly facilitated substrate diffusion. When loaded with FeT_{NH₂}PPBr, NbSi4-20 with 33 Å pores led to significantly higher epoxide selectivity (78.9%) than NbSil-5.4 (24 Å pores, 58.2% selectivity). Cyclohexene conversions over these two supported catalysts were similar after 2 h, even though a lower FeT_{NH₂}PPBr loading was employed in NbSi4-20.

We also examined cyclooctene as a substrate that is less prone to O₂ oxidation than cyclohexene. Unlike cyclohexene, the selectivity to epoxide was 100% in the oxidation of cyclooctene. The conversion after 5 h of reaction was higher for FeT_{NH₂}PPBr/NbSil-5.4 than for FeT_{NH₂}PPBr/NbSil-11.4, as the higher Nb dopant concentration of the former allowed for a greater maximum metalloporphyrin loading level (Table 1). However, TON decreased with increased metalloporphyrin loading in the NbSil-R supports, suggesting that not all the metalloporphyrin sites were accessible to the bulky substrates for epoxidation catalysis, possibly due to the pore size constraint of the support matrix (23–24 Å).

The effect of support pore size on catalytic conversion of cyclooctene was examined systematically to investigate the role of diffusional restriction in the heterogenized catalysts. Among the various systems examined, FeT_{NH₂}PPBr supported on sol-gel derived amorphous Nb-doped silica showed the lowest activity after 5 h (14% conversion, TON = 11). This could be attributed to steric constraints within this microporous support. With an identical Fe loading of 0.36 mg, mesoporous NbSil-11.4 provided 3 times greater activity (42% conversion, TON = 33) than microporous Nb-doped silica gel. Using mesoporous NbSi4-20, which has a larger pore size (33 Å) than NbSil-11.4 (23 Å), 98% epoxidation of cyclooctene was achieved in < 5 h despite the lower Fe loading (0.14 mg). An excellent TON of 196 was achieved over FeT_{NH₂}PPBr/NbSi4-20, which was even higher than that attained by the homogeneous FeT_{NH₂}PPBr system (TON = 170). For both FeT_{NH₂}PPBr/NbSi4-20 and unsupported FeT_{NH₂}PPBr, a similar catalyst loading of 0.14 mg Fe was introduced to the reactant solution. The greater TON over FeT_{NH₂}PPBr/NbSi4-20 suggested that highly dispersed

iron porphyrins fixated within supports of sufficiently large pore dimensions would have no diffusional constraints that inhibit substrate conversion, while preventing the detrimental self-oxidation of metalloporphyrins experienced in homogeneous systems. Our studies clearly showed that the support microstructure and iron porphyrin loading were important factors governing the catalyst performance.

During the course of the oxidation reactions, no catalyst leaching was detected in our systems, as indicated by the absence of the characteristic Soret band associated with free Fe(III)T_{NH₂}PPBr in the UV–VIS spectra of the reaction solutions. This confirmed that Fe(III)T_{NH₂}PPBr was stably immobilized within the porous Nb-doped silicate framework *via* the N–Nb ligand interaction. We further examined catalytic performance over multiple oxidation cycles, and found no degradation in conversion over our supported catalyst systems for at least three oxidation cycles. These studies demonstrated the effectiveness of heterogenizing catalysts through strong catalyst–support interactions, which could be established easily *via* appropriate doping of the porous support. The flexibility of pore size tailoring in Nb-doped mesoporous silicates further enabled us to optimize the activity of supported iron porphyrins by providing full accessibility to the catalytic sites. Such catalyst design considerations can be applied broadly to achieve heterogenized catalysts of bulky, stereospecific enzyme and organometallic complexes for effective and efficient synthesis of fine chemicals and pharmaceuticals.

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Notes and references

† Synthesis of NbSi4-R. 5 mmol of CTAB and 2.5 mmol of tetradecylamine (Acros) were first dissolved in 108 g of water. 11.4 g of tetraethoxysilane (United Chemical) were gradually added to the surfactant solution at room temp. and stirred for 30 min. A measured amount of niobium ethoxide was then introduced dropwise into the loosley-bonded silica gel. The resulting gel mixture was adjusted to pH 11 with the addition of tetraethylammonium hydroxide, and stirred for 3 h at ambient conditions before subjected to hydrothermal treatment at 120 °C for 4 days.

- 1 D. Ostovic, G. S. He and T. C. Bruice, in *Metalloporphyrins in Catalytic Oxidations*, ed. R. A. Sheldon, Marcel Dekker, New York, 1994, ch. 2.
- 2 B. Meunier, *Chem. Rev.*, 1992, **92**, 1411.
- 3 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710; A. Monnier, F. Schüth, Q. Huo, D. Kumar, D. I. Margolese, R. S. Maxwell, G. D. Stucky, M. Krishnamurthy, P. Petroff, A. Firouzi, M. Janicke and B. F. Chmelka, *Science*, 1993, **261**, 1299; P. T. Tanev and T. J. Pinnavaia, *Science*, 1995, **267**, 865; H. Yang, A. Kuperman, N. Coombs, S. Mamiche-Afara and G. A. Ozin, *Science*, 1996, **379**, 703.
- 4 C.-J. Liu, S.-G. Li, W.-Q. Pang and C.-M. Che, *Chem. Commun.*, 1997, 65; C.-J. Liu, W.-Y. Yu, S.-G. Li and C.-M. Che, *J. Org. Chem.*, 1998, **63**, 7364.
- 5 B. T. Holland, C. Walkup and A. Stein, *J. Phys. Chem. B*, 1998, **102**, 4301.
- 6 D. M. Antonelli and J. Y. Ying, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 426; D. M. Antonelli, A. Nakahira and J. Y. Ying, *Inorg. Chem.*, 1996, **35**, 3126; D. M. Antonelli and J. Y. Ying, *Chem. Mater.*, 1996, **8**, 874; T. Sun and J. Y. Ying, *Nature*, 1997, **389**, 704.
- 7 L. Zhang and J. Y. Ying, *AIChE J.*, 1997, **43**, 2793.
- 8 J. Collman, R. R. Gagne, C. A. Reed, T. R. Halbert, G. Lang and W. T. Robinson, *J. Am. Chem. Soc.*, 1975, **97**, 1427.
- 9 P. Rothemund, *J. Am. Chem. Soc.*, 1939, 2012.
- 10 J. T. Groves and D. V. Subramanian, *J. Am. Chem. Soc.*, 1984, **106**, 2177.
- 11 D. R. Leanord and J. R. Lindsay Smith, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1917.

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